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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Calcind Hydrotalcites as Catalysts for Ethoxylating or
Propoxylating Fatty Acid Esters

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Notice: The specification contained herein as filed

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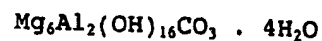
CCA 3254 (10-89) 41

27 April 1989

5 Use of calcined hydrotalcites as catalysts for the ethoxylation or propoxylation of fatty acid esters.

The invention relates to the use of calcined hydrotalcites as catalysts for the ethoxylation or propoxylation of fatty acid esters selected from the group formed by esters of optionally hydroxy-substituted fatty acids having 8 to 22 carbon atoms with monoalkanols having 1 to 22 carbon atoms, and by partial esters and full esters of optionally hydroxy-substituted fatty acids having 8 to 22 carbon atoms with polyols having 2 to 12 carbon atoms and 2 to 6 hydroxyl groups.

15 Hydrotalcite is a natural mineral having the ideal formula



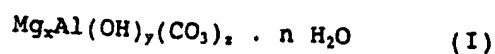
the structure of which is derived from that of brucite ($\text{Mg}(\text{OH})_2$). Brucite crystallizes in a layer structure with the metal ions in octahedral vacancies between two layers of closely packed hydroxyl ions, only every second layer of the octahedral vacancies being occupied. In hydrotalcite, some magnesium ions are replaced by aluminum ions, which gives the layer package a positive charge. This is compensated by the anions present in the intermediate layers together with zeolitic water of crystallization. The layer structure is clearly visible in the X-ray powder diagram (ASTM card No. 14-191), which can be used for characterization.

30 Synthetically prepared hydrotalcites are also known and are described, for example, in DE-C 1,592,126, DE-A 3,346,943, DE-A 3,306,822 and EP-A 0,207,811.

35 In natural and synthetic products, the $\text{Mg}^{2+}:\text{Al}^{3+}$ ratio can vary between about 1 and 5. The $\text{OH}^-:\text{CO}_3^{2-}$ ratio can also vary. Natural and synthetic hydrotalcites can be

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described approximately by the general formula I



where the conditions $1 < x < 5$, $y > z$, $(y + 0.5z) = 2x + 3$ and $0 < n < 10$ apply. Differences in the composition of the hydrotalcites, in particular with respect to the water content, result in line shifts in the X-ray diffraction diagram.

Natural or synthetic hydrotalcites continuously release water on heating or calcination. The dehydration is complete at 200°C, when it can be shown, by X-ray diffraction, that the structure of the hydrotalcite has been retained. A further increase in temperature results in degradation of the structure with elimination of hydroxyl groups (as water) and of carbon dioxide. Natural hydrotalcites and those prepared synthetically by various processes, for example in accordance with the above publications, exhibit a generally similar behavior on calcination.

Calcined hydrotalcites have already been employed for various purposes, for example as absorbents and in reactions of alkylene oxides with alkyl acetates to prepare mono-, di- and triethylene glycol ethyl ether acetates, cf. JP-A 56/36,431, cited in C.A. 95(11)97 099m (1981).

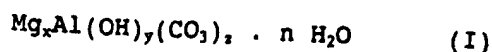
For polyalkoxylates, a narrow range of the degree of polyalkoxylation is of particular importance, cf. JAACS, Vol. 63, 691-695 (1986), and HAPPI, 52-54 (1986).

It has now been found that calcined hydrotalcites can be used according to the invention as catalysts to polyalkoxylate fatty acid esters of the type mentioned in the introduction in high yields and in short reaction times to give reaction products having a narrower polyalkoxylation range or homolog distribution than can be obtained when the sodium methoxide usually employed as catalyst is used.

For the purposes of the invention, all catalysts which can be obtained by calcination from the natural

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and/or synthetic hydrotalcites mentioned in the introduction are suitable; hydrotalcites which, before calcination, have the general formula I



5 with the abovementioned conditions for x, y, z and n are preferred; values for x of from 1.8 to 3 are particularly preferred.

10 The calcined hydrotalcites employed according to the invention have the advantage that they can easily be incorporated into the alkoxylation reaction mixture and can be separated off again by simple measures due to their insolubility in the reaction mixture. However, they may also remain in the reaction mixture if their presence does not interfere with the further use of the reaction products.

15 Examples of fatty acid esters of the type mentioned in the introduction which can be alkoxyated, according to the invention, using calcined hydrotalcites are listed below, the fatty acid component of the fatty acid esters being listed first and the alcohol component thereof then being listed separately.

Fatty acids:

20 Fatty acids having 8 to 22 carbon atoms of natural or synthetic origin, in particular straight-chain, saturated or unsaturated fatty acids, including technical-grade mixtures thereof, as can be obtained by lipolysis from animal and/or vegetable fats and oils, for example from coconut oil, palm kernel oil, palm oil, soya oil, sunflower oil, rapeseed oil, cottonseed oil, fish oil, beef tallow and lard; specific examples are caprylic acid, capric acid, lauric acid, lauroleic acid, myristic acid, myristoleic acid, palmitic acid, palmitoleic acid, oleic acid, elaidic acid, arachidic acid, gadoleic acid, behenic acid, brassidic acid and erucic acid; furthermore
25 methyl-branched, saturated and unsaturated fatty acids having 10 to 22 carbon atoms, which are produced as by-products in the dimerization of the corresponding unsaturated
30

turated fatty acids.

Hydroxyfatty acids:

Natural or synthetic hydroxyfatty acids, in particular having 16 to 22 carbon atoms, for example ricinoleic acid or 12-hydroxystearic acid.

Alkanols:

Saturated or unsaturated monoalkanols, in particular products of hydrogenation of the abovementioned straight-chain, saturated or unsaturated fatty acids or derivatives thereof, such as methyl esters or glycerides; aliphatic or cyclic alkanols having 1 to 6 carbon atoms, for example methanol, ethanol, propanol, butanol, hexanol and cyclohexanol; including the Guerbet alcohols derived from the abovementioned monoalkanols.

Polyols:

Ethylene glycol, 1,2-propylene glycol, 1,2-butylene glycol, neopentyl glycol, glycerol, diglycerol, triglycerol, tetraglycerol, trimethylolpropane, di-trimethylolpropane, pentaerythritol, di-pentaerythritol, and sugar alcohols, in particular sorbitan.

As stated in the introduction, the esters of the above fatty acids with the abovementioned polyols may also be in the form of partial esters or partial ester-containing technical-grade ester mixtures, in particular in the form of glycerides.

The structure of the ethoxylated or propoxylated fatty acid esters obtained according to the invention cannot always be determined unambiguously. Fatty acid monoalkanol esters and fatty acid polyol full esters react - with a high probability of an insertion of the ethyleneoxy and/or propyleneoxy units into the ester bond - to give essentially hydroxyl group-free end products. The structure of the hydroxyl group-containing products which result from the reaction of polyol partial esters of fatty acids with ethylene oxide and/or propylene oxide is unknown for the time being; here, reactions at the free OH groups are also conceivable, in particular in the case of free primary OH groups.

The derivatives to be prepared according to the

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inv ntion using calcined hydrotalcites are commrcial products, so more detailed d scription is superfluous. Typical representatives of these derivatives are, for example, products of the adduction of 41 moles of ethylene oxide with castor oil, products of the adduction of 25 moles of ethylene oxide with hardened castor oil, products of the adduction of 7 parts by weight of ethylene oxide with 10 parts by weight of a palmitic acid/stearic acid monoglyceride/diglyceride mixture containing 40 to 45% by weight of monoglyceride, and products of the adduction of 20 moles of ethylene oxide with sorbitan monostearate.

According to a further advantageous embodiment of the invention, the calcined hydrotalcites are added to the reaction mixtures in an amount of from 0.1 to 2% by weight, relative to the end product of the ethoxylation or propoxylation.

The calcined hydrotalcites to be employed according to the invention can be obtained from natural or synthetic hydrotalcites by heating for several hours at temperatures of greater than 100°C; calcination temperatures of from 400 to 600°C are particularly preferred.

The invention is illustrated in greater detail below with reference to preferred illustrative examples and a comparison example.

Example 1.

Castor oil + 1.4 mol of ethylene oxide.

A commercial synthetic hydrotalcite was calcined for 4 hours at 500°C.

In order to react a commercial castor oil with 1.4 mol of ethylene oxide, the castor oil was introduced into a pressure reactor, and 0.5% by weight, relative to the expected end product, of the previously obtained calcined hydrotalcite was added. The reactor was flushed with nitrogen and evacuated for 30 minutes at a temperature of 100°C. The temperature was subsequently

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increased to 165 - 175°C, and the desired amount of ethylene oxide was injected at a pressure of from 3 to 5 bar. When the reaction was complete, a post-reaction time of 30 minutes was allowed (total reaction time: 3 hours). After the suspended catalyst had been filtered off, the reaction mixture desired, having a saponification number of 155 (theor.: 138), was obtained.

Example 2.

Methyl laurate + 2 mol of ethylene oxide.

Under the conditions indicated in Example 1, a commercial methyl laurate and 2 mol of ethylene oxide gave, after a reaction time of 0.75 hour, the desired product having a saponification number of 185 (theor.: 185.7).

Example 3.

Rapeseed oil + 3 mol of ethylene oxide.

Under the conditions indicated in Example 1, a commercial rapeseed oil gave the abovementioned ethoxylation product having a saponification number of 150 (theor.: 130). The total reaction time was 2.5 hours.

Comparison example.

Example 2 was repeated, but the calcined hydrotalcite employed therein was replaced by sodium methoxide as the catalyst. The composition of the ethoxylation product obtained was determined by gas chromatography (in area percent), and compared with that of the product from Example 2; the results are summarized in the table below. The term "EO degree" indicates the number of ethylene oxide molecules adducted with methyl laurate, a degree of ethoxylation of 0 denoting unreacted starting material.

The table shows that the amount of unreacted starting material in the product of the comparison example is higher by a factor of 2 and the amount of desired end product is more than 3 times lower than in the product of Example 2.

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Table

Homolog distribution in the
ethoxylation of methyl laurate

5	EO degree	Example 2	Comparison example	
			(area percent)	
	0	31.3		60.0
	1	12.1		11.2
	2	14.1		4.2
10	3	12.2		3.3
	4	9.6		3.0
	5	5.8		4.2
	6	4.3		2.8
	7	3.2		2.6
15	8	2.4		2.3
	9	1.8		2.0
	10	1.4		1.7
	11	0.9		1.2
	12	0.6		0.9

Henkel Kommanditgesellschaft auf Aktien
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P 13299/89
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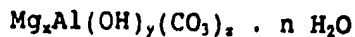
Patent claims

1. The use of a calcined hydrotalcite as catalyst for the ethoxylation or propoxylation of fatty acid esters selected from the group formed by esters of optionally hydroxy-substituted fatty acids having 8 to 22 carbon atoms with monoalkanols having 1 to 22 carbon atoms, and by partial esters and full esters of optionally hydroxy-substituted fatty acids having 8 to 22 carbon atoms with polyols having 2 to 12 carbon atoms and 2 to 6 hydroxyl groups.
2. The use as claimed in claim 1, wherein saturated or unsaturated fatty acid C₁-C₄-alkyl esters are ethoxylated or propoxylated.
3. The use as claimed in claim 1 or 2, wherein glycerides of optionally monohydroxy-substituted, saturated or unsaturated fatty acids are ethoxylated or propoxylated.
4. The use as claimed in at least one of claims 1 to 3, wherein the hydrotalcite, before calcination, has a composition of the formula I



in which the conditions $1 < x < 5$, $y > z$, $(y + 0.5 z) = 2x + 3$ and $0 < n < 10$ apply.

5. The use as claimed in at least one of claims 1 to 4, wherein, for the hydrotalcite of the general formula I



x is a number from 1.8 to 3, and y, z and n are as defined above.

6. The use as claimed in at least one of claims 1 to 5, wherein the hydrotalcite had been calcined at a temperature between 400 and 600°C.

7. The use as claimed in at least one of claims 1 to 6, wherein the calcined hydrotalcite is employed in an amount of from 0.1 to 2% by weight, relative to the end product of the ethoxylation or propoxylation.

Use of calcined hydrotalcites as catalysts for the
ethoxylation or propoxylation of fatty acid esters

Abstract of the disclosure

Calcined hydrotalcites, as catalysts for the ethoxylation or propoxylation of fatty acids having 8 to 22 carbon atoms with monoalkanols having 1 to 22 carbon atoms or polyols having 2 to 6 hydroxyl groups and 2 to 15 carbon atoms, give the desired products in high yields and with a narrow range of the homolog distribution of the ethoxylation or propoxylation products.